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# A new *ab initio* potential energy surface for the collisional excitation of $\text{N}_2\text{H}^+$ by $\text{H}_2$

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We compute a new potential energy surface (PES) for the study of the inelastic collisions between  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  molecules. A preliminary study of the reactivity of  $\text{N}_2\text{H}^+$  with  $\text{H}_2$  shows that neglecting reactive channels in collisional excitation studies is certainly valid at low temperatures. The four dimensional (4D)  $\text{N}_2\text{H}^+-\text{H}_2$  PES is obtained from electronic structure calculations using the coupled cluster with single, double, and perturbative triple excitation level of theory. The atoms are described by the augmented correlation consistent triple zeta basis set. Both molecules were treated as rigid rotors. The potential energy surface exhibits a well depth of  $\approx 2530\text{ cm}^{-1}$ . Considering this very deep well, it appears that converged scattering calculations that take into account the rotational structure of both  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  should be very difficult to carry out. To overcome this difficulty, the “adiabatic-hindered-rotor” treatment, which allows para- $\text{H}_2(j=0)$  to be treated as if it were spherical, was used in order to reduce the scattering calculations to a 2D problem. The validity of this approach is checked and we find that cross sections and rate coefficients computed from the adiabatic reduced surface are in very good agreement with the full 4D calculations. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4923440>]

## I. INTRODUCTION

Modelling of physical and chemical conditions in the interstellar clouds requires to model the emission of various molecular species (neutrals, ions, or radicals). Several molecules can be used to probe different physical conditions of the molecular clouds. However, dense molecular clouds, and especially prestellar cores, suffer from strong depletion of most of the usual tracers (CO, CS, SO, etc., e.g., Ref. 1) and it has been found that only a few species survive in the gas phase. Among them, nitrogen bearing molecules are the best known ( $\text{NH}_3$ ,  $\text{N}_2\text{H}^+$ , or  $\text{CN}^{2-5}$ ).

$\text{N}_2\text{H}^+$  was one of the first molecular ions detected in the interstellar medium (ISM).<sup>6</sup> Most observations concern the  $j=1 \rightarrow 0$  line, whose hyperfine structure helps to discriminate between opacity effects and collisional excitation effects, and thus, to study the deeper regions of cold cores contrarily to other species with larger opacities. However, to fully use the capabilities of  $\text{N}_2\text{H}^+$  as a tracer of dense cloud conditions, state-to-state collisional data are needed.<sup>7</sup>

In addition, along with CN and HCN molecules,  $\text{N}_2\text{H}^+$  is also used to determine  $^{14}\text{N}/^{15}\text{N}$  abundance ratio in the universe.<sup>8</sup>  $^{15}\text{N}$ -fractionation can have strong implications for our understanding of the diversity observed in the various

bodies of the solar system. In cold dark clouds,  $^{14}\text{N}/^{15}\text{N}$  abundance ratio is presently poorly constraint and the ratio varies from 150 to 1000 depending on the molecules and on the astronomical sources.<sup>8-10</sup> An important source of inaccuracies comes from the uncertainties linked with the  $\text{N}_2\text{H}^+$  rate coefficients.

As a consequence, the determination of rate coefficients for collisions between the  $\text{N}_2\text{H}^+$  ( $X^1\Sigma^+$ ) molecule and the most abundant interstellar species (He and  $\text{H}_2$ ) has been one of the important goals of molecular astrophysics in the past decades. The first  $\text{N}_2\text{H}^+-\text{He}$  rate coefficients were provided by Green<sup>11</sup> in 1975. More recently, Daniel *et al.*<sup>12,13</sup> have computed a new  $\text{N}_2\text{H}^+-\text{He}$  potential energy surface (PES) from highly correlated *ab initio* calculations and derived the corresponding rotational excitation rate coefficients. These last results differ within a few percent up to 100% from the former calculations by Green.<sup>11</sup> Cross sections and rate coefficients between hyperfine levels were then obtained using a recoupling technique.<sup>13</sup> In the absence of data with the  $\text{H}_2$  collisional partner, He rate coefficients are generally used as a model for the  $\text{H}_2$  ones.<sup>14,15</sup>

However, the necessity to compute exact  $\text{H}_2$  rate coefficients and not using He ones as an estimate, particularly when the target is an ion, has been pointed out.<sup>7</sup> It is then crucial to provide the astronomical community with reliable  $\text{N}_2\text{H}^+-\text{H}_2$  rate coefficients. Compared to the case of collisions with rare gas atoms, the increasing difficulty to consider  $\text{H}_2$  as

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collider lies not only in the higher dimensionality of the system but also in the possibility for the interacting species to form chemical bonds and react. Indeed, during the collisions between  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  molecules, inelastic and reactive collisions can compete. Hence, one has to check first that the probability of reactive collisions is very low compared to inelastic collisions due to an activation barrier or due to a significant endothermicity.

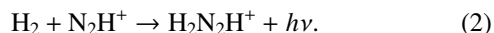
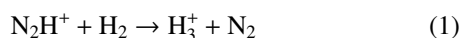
In this paper, we report first a preliminary study of the reactive pathways in order to check the barrier heights and endothermicity for the  $\text{N}_2\text{H}^+ + \text{H}_2$  reactive collisions. This is followed by highly correlated *ab initio* calculations of the  $\text{N}_2\text{H}^+-\text{H}_2$  PES. Taking into account the huge well depth found for the  $\text{N}_2\text{H}^+-\text{H}_2$  interaction as well as the small rotational constant of the  $\text{N}_2\text{H}^+$  molecule, converged scattering calculations are anticipated to be very challenging from a CPU point of view. As a consequence, in the third part of the paper, the “adiabatic-hindered-rotor” (AHR) treatment which allows para- $\text{H}_2$  ( $j = 0$ ), the main collisional partner in the cold ISM, to be treated as if it were spherical is explored in order to reduce the scattering calculations to a 2D problem.

This paper is organized as follows. In Sec. II, we explore the reactive path during  $\text{N}_2\text{H}^+ + \text{H}_2$  collisions. Sec. III describes the *ab initio* calculations of the  $\text{N}_2\text{H}^+-\text{H}_2$  PES and its analytical representation. In Sec. IV, we use the AHR method to separate the rotation of hydrogen from the other degrees of freedom. Section V is devoted to the validation of the reduced dimension approach. Conclusions are finally drawn in Section VI.

## II. REACTIVITY STUDY

As mentioned in the Introduction,  $\text{N}_2\text{H}^+ + \text{H}_2$  collisions can be either inelastic or reactive collisions. At low temperatures, it can be anticipated that the reaction to form  $\text{H}_3^+ + \text{N}_2$  is inefficient. Otherwise,  $\text{N}_2\text{H}^+$  would not be easily detected. However, it is crucial to determine the temperature range where the reaction is inhibited in order to determine the validity area of a collisional study considering only the collisional excitation processes.

Hence, calculations have been performed, using GAUSSIAN 09,<sup>16</sup> to determine the region where the  $\text{N}_2\text{H}^+$  cation does not react with molecular hydrogen. Thus, we have explored two possible reactive channels,



Reaction (2) corresponds to a radiative association reaction. Radiative association reactions may be efficient in the cold ISM.

The first process is clearly endothermic favoring the formation of  $\text{N}_2\text{H}^+$  from  $\text{H}_3^+$  and  $\text{N}_2$  and not the destruction of  $\text{N}_2\text{H}^+$  due to collisions with  $\text{H}_2$ . Based on the explicitly correlated spin-restricted coupled cluster method with single, double, and perturbative triple excitations and the augmented correlation-consistent triple zeta basis set (RCCSD(T)-F12/aug-cc-pVTZ),<sup>17,18</sup> the enthalpy is calculated to be  $\Delta H \approx 6300 \text{ cm}^{-1}$ . Reaction (1) is then expected not to proceed at

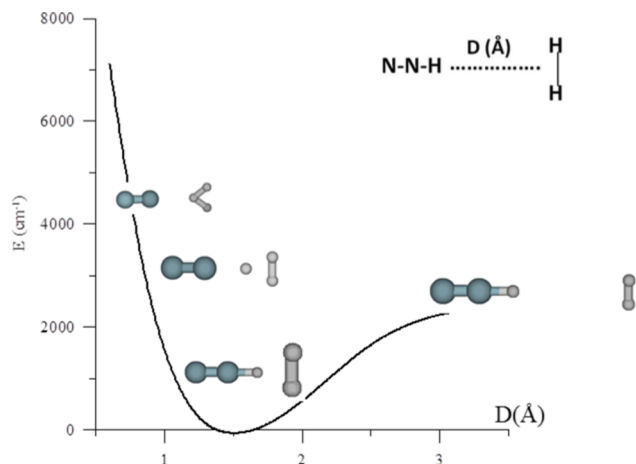


FIG. 1. The minimum energy pathway for the perpendicular attack. The minimum of the curve ( $E = 0.0 \text{ cm}^{-1}$ ) corresponds to  $D = 1.455 \text{ Å}$ ;  $NN = 1.0918 \text{ Å}$ ;  $NH = 1.0787 \text{ Å}$ ;  $HH = 0.7570 \text{ Å}$ .

low and intermediate collisional energies that are encountered in the ISM.

Using CCSD/aug-cc-pVTZ level of theory, the minimum energy pathways considering the  $\text{H}_2$  molecule approaching perpendicular or parallel to the  $\text{N}_2\text{H}^+$  principal axis have been computed. For this purpose, the total electronic energies have been calculated for different values of the  $D$  reaction coordinate (see Figs. 1 and 2). The remaining internal coordinates of the complex have been optimized.

Figures 1 and 2 display the one-dimensional potential energy curves. In Fig. 1, the  $D$  independent coordinate has been defined as the distance between the center of mass of the  $\text{H}_2$  molecule and the hydrogen atom of  $\text{N}_2\text{H}^+$ . In Fig. 2,  $D$  represents the distance between the  $\text{N}_2\text{H}^+$  hydrogen and one of the  $\text{H}$  atoms of the  $\text{H}_2$  molecule. It can be inferred that the formation of  $\text{N}_2\text{H}^+$  from  $\text{H}_3^+ + \text{N}_2$  is not restricted by any barrier.

The second process is studied following the same procedure as described above, the minimum energy pathway being determined at the second-order Møller Plesset perturbation (MP2/aug-cc-pVTZ) level of theory. The formation of

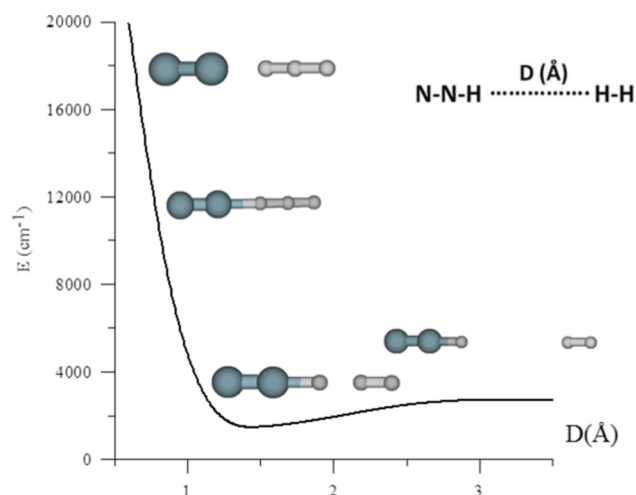


FIG. 2. The minimum energy pathway for the perpendicular attack. The minimum of the curve ( $E = 2038 \text{ cm}^{-1}$ ) corresponds to  $D = 1.6048 \text{ Å}$ ;  $NN = 1.0914 \text{ Å}$ ;  $NH = 1.0446 \text{ Å}$ ;  $HH = 0.7447 \text{ Å}$ .

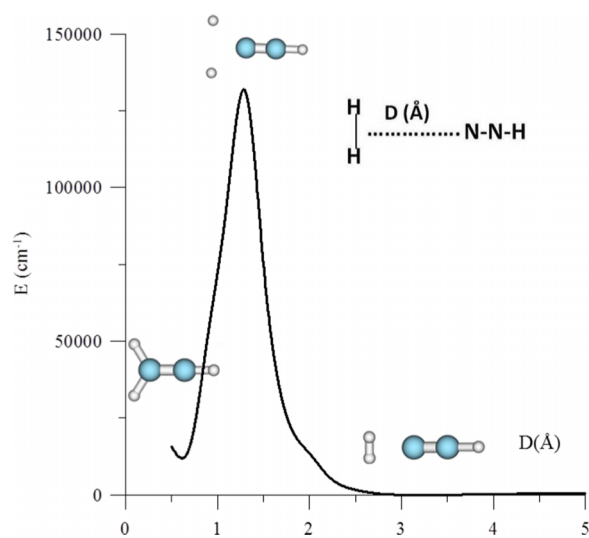


FIG. 3. The minimum energy path for reaction 2.

a  $\text{H}_2\text{N}_2\text{H}^+$  complex is also endothermic (see Fig. 3). With the MP2/aug-cc-pVTZ, the enthalpy has been calculated to be  $\Delta H \approx 14\,800\text{ cm}^{-1}$ . In addition, a high potential barrier prevents the process. The barrier corresponds to the breaking of the  $\text{H}_2$  molecule bond.

This study confirms that the formation of the diazenium ion ( $\text{N}_2\text{H}_3^+$ ) is strongly endothermic as already noticed in Ref. 19 and that neglecting reactive channels for the study of collisional excitation of  $\text{N}_2\text{H}^+$  by  $\text{H}_2$  is valid at the typical temperatures of the ISM.

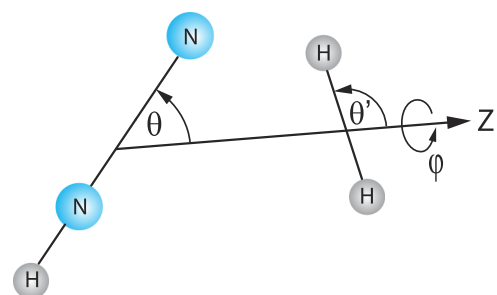
### III. AB INITIO CALCULATIONS

Once it has been determined that inelastic collisions can be safely studied without considering the reactive pathways, we compute a PES for the rotational excitation of  $\text{N}_2\text{H}^+$  by  $\text{H}_2$ .

#### A. Ab initio calculations of the PES

At typical interstellar temperatures, ( $T \leq 300\text{ K}$ ), molecules like  $\text{N}_2\text{H}^+$  are generally in their ground vibrational state. The lowest vibrational bending frequency of  $\text{N}_2\text{H}^+$  is  $\nu_2 = 627.7\text{ cm}^{-1}$ .<sup>20</sup> The probability of vibrational excitation is very low and can be neglected in the scattering calculations. As a first guess, the collision partners may thus be considered as rigid. However, according to the large well depth found in the  $\text{N}_2\text{H}^+-\text{H}_2$  PES (see Figs. 1 and 2), vibrational couplings may not be negligible even at low collisional energies. In addition, further dynamics calculations may span a range of energies which pass the threshold of the  $\nu_2$  bending mode ( $627.7\text{ cm}^{-1}$ ) so that the rigid rotor approximation may be questionable.

In a recent study of the  $\text{HCN}-\text{He}$  system,<sup>21</sup> it has been shown that accounting for the bending motion during the collision affects weakly rotational excitation of the molecule compared to the rigid-rotor case, even when excited bending mode is energetically accessible. Moreover, in another recent study<sup>22</sup> on the collisional excitation of  $\text{OH}^+$  by  $\text{H}$  (also a reactive system with a large endothermicity), it has been found

FIG. 4. The body-fixed Jacobi coordinates system for the  $\text{N}_2\text{H}^+-\text{H}_2$  complex.

that exact close coupling calculations (including the reactive channels) were in good agreement with rigid rotor calculations. Hence, we believe that using a rigid rotor approach for studying the rotational excitation of  $\text{N}_2\text{H}^+$  by  $\text{H}_2$  will be accurate enough for astrophysical purpose as far as the temperatures remain low.

The  $\text{N}_2\text{H}^+$  molecule in its ground electronic state has a linear equilibrium structure. The  $\text{H}_2$  molecule was also considered as rigid. The body-fixed coordinate system used in the calculations is shown in Fig. 4. The geometry of the  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  complex is characterized by three angles  $\theta$ ,  $\theta'$ , and  $\varphi$  and the distance  $R$  between the centers of masses of  $\text{N}_2\text{H}^+$  and  $\text{H}_2$ . The polar angles of  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  with respect to the  $z$ -axis that coincides with  $\vec{R}$  are denoted, respectively, by  $\theta$  and  $\theta'$ , while  $\varphi$  denotes the dihedral angle between half-planes containing the  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  bonds. As shown previously,<sup>23</sup> a better description of the intermolecular potential is obtained by fixing the molecular distance at its average value in the ground vibrational level rather than at the equilibrium distance. Accordingly, we used a  $\text{H}_2$  bond distance of  $r_{\text{HH}} = 1.448\text{ a}_0$ . Since such data are not available for  $\text{N}_2\text{H}^+$ , we chose internuclear distances fixed at their experimental equilibrium values:<sup>24</sup>  $r_{\text{NN}} = 2.065\text{ a}_0$  and  $r_{\text{NH}} = 1.955\text{ a}_0$ .

*Ab initio* calculations of the four dimensional (4D)  $\text{N}_2\text{H}^+-\text{H}_2$  PES were carried out at the coupled cluster with single, double, and perturbative triple excitation [CCSD(T)]<sup>25,26</sup> level of theory using the MOLPRO 2010 package.<sup>27</sup>

Preliminary calculations have shown that an accurate description of both  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  rotations has implied to compute the interaction potential for a large number of geometries. Then, the choice of the atomic basis set implies a compromise between accuracy and CPU time. We have performed interaction energy calculations for the  $\text{N}_2\text{H}^+-\text{H}_2$  system with selected geometries using the aug-cc-pVXZ ( $X = \text{T, Q, 5}$ ) basis sets of Woon and Dunning.<sup>28</sup> Figure 5 presents a comparison of the performance of the various basis sets.

As can be seen, differences exist between results obtained using aVTZ, aVQZ, and aV5Z basis sets, the difference being around 5%-10% in the well area. However, as found previously,<sup>29</sup> inelastic rate coefficients (contrary to scattering resonances) are not highly sensitive to the potential well depth. Hence, we decide to limit the size of the basis set to aVTZ to maintain reasonable CPU time considering that the accuracy of the corresponding rate coefficients will be enough for astrophysical purpose. Note that the agreement between results obtained with the three basis sets increases with increasing radial coordinate  $R$  and that the accuracy of the PES obtained



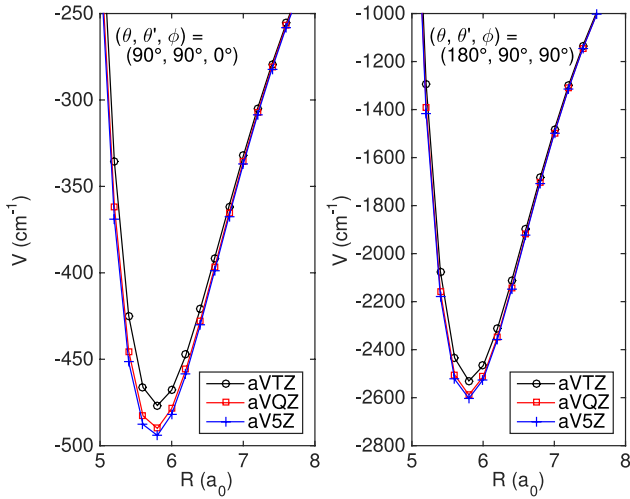


FIG. 5. Comparison of the performance of various basis sets in the calculation of the interaction energy of the  $\text{N}_2\text{H}^+-\text{H}_2$  complex, for a few combinations of angular parameters  $(\theta, \theta', \phi)$ .

using the aVTZ basis set is very good in the long range as it will be also demonstrated below.

The radial scattering coordinate  $R$  was assigned 48 values from  $4.0 a_0$  to  $40 a_0$ , the  $\theta$  grid ranged from  $0^\circ$  to  $180^\circ$  in steps of  $15^\circ$ , whereas  $\theta'$  and  $\varphi$  ranged from  $0^\circ$  to  $180^\circ$  and  $0^\circ$  to  $90^\circ$ , respectively, in steps of  $30^\circ$ . The geometry with  $\theta = 0^\circ$  and  $\theta' = 0^\circ$  corresponds to  $\text{H}-\text{N}-\text{N}^+ \cdots \text{H}-\text{H}$  geometry.

In all calculations, the basis set superposition error (BSSE) was corrected at all geometries with the Boys and Bernardi<sup>30</sup> counterpoise correction scheme,

$$V(R, \theta, \theta', \varphi) = E_{\text{N}_2\text{H}^+-\text{H}_2}(R, \theta, \theta', \varphi) - E_{\text{N}_2\text{H}^+}(R, \theta, \theta', \varphi) - E_{\text{H}_2}(R, \theta, \theta', \varphi), \quad (3)$$

where the energies of  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  subsystems are computed with the full basis set.

The  $R$ -dependence of the  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  interaction energy for  $\theta = 0^\circ, 90^\circ, 180^\circ$  is displayed in Fig. 6 for several  $(\theta', \varphi)$  orientations. A very strong anisotropy as a function of the  $\text{H}_2$  orientation is observed.

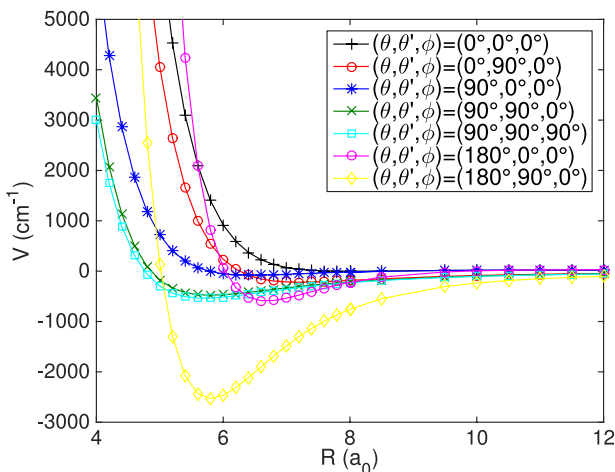


FIG. 6. Plot of the radial dependence of the CCSD(T) interaction energy for seven orientations. Energy is in  $\text{cm}^{-1}$ .

## B. Analytical representation

In order to provide the potential for a wide range of intermolecular separations, we have performed analytical calculations of interaction energy on the basis of multipolar expansion. In the framework of the long-range approximation,<sup>31</sup> the interaction energy of the  $\text{N}_2\text{H}^+-\text{H}_2$  system is a sum of the electrostatic ( $E_{\text{elec}}$ ), induction ( $E_{\text{ind}}$ ), and dispersion ( $E_{\text{disp}}$ ) contributions. As the  $\text{N}_2\text{H}^+$  molecule has a charge, we will limit the multipolar expansion to terms through the order of  $R^{-4}$  (we will neglect the dispersion interactions which vary as  $R^{-6}$ ),

$$E_{\text{elec}} = \frac{1}{3} T_{\alpha\beta} \Theta_{\alpha\beta}^B q^A - \frac{1}{3} T_{\alpha\beta\gamma} \Theta_{\alpha\beta}^B \mu_\gamma^A. \quad (4)$$

$$E_{\text{ind}} = -\frac{1}{2} T_\alpha T_\beta \alpha_{\alpha\beta}^B (q^A)^2. \quad (5)$$

Superscripts  $A$  and  $B$  denote molecules  $\text{N}_2\text{H}^+$  and  $\text{H}_2$ , accordingly. Tensor  $T_{\alpha\beta\cdots} = \nabla_\alpha \nabla_\beta \cdots R^{-1}$  is the symmetric tensor relative to the permutation of any pair of subscripts. There is a summation over the repeated indexes.

The charge ( $q^A$ ) of  $\text{N}_2\text{H}^+$  molecule is equal to 1 a.u. The dipole ( $\mu$ ) and quadrupole ( $\Theta$ ) moments as well as static dipole polarizability ( $\alpha$ ) of monomers were calculated at the CCSD(T) level of theory with aVTZ basis set using the finite-field approach.<sup>32</sup> The quadrupole moment of hydrogen molecule is  $\Theta_{zz} = 0.486$  a.u. (experimental value is 0.46 a.u.<sup>33</sup>) and the polarizability components are  $\alpha_{xx} = \alpha_{yy} = 4.76$  and  $\alpha_{zz} = 6.73$  a.u. Our average value of  $\alpha = 1/3(2\alpha_{xx} + \alpha_{zz}) = 5.42$  a.u. agrees with experimental  $\alpha = 5.42$  a.u.<sup>34</sup> The dipole moment of  $\text{N}_2\text{H}^+$  molecule was calculated to be  $\mu_z = -1.33$  a.u. which is in excellent agreement with the value  $-1.34 \pm 0.20$  from Ref. 35. The sign of dipole moment corresponds to the alignment of the molecule along  $z$ -axis with H atom pointing to the negative direction. It should be noted that all properties in Eqs. (4) and (5) are represented in the coordinate system of a complex, i.e., the above presented molecular properties should be appropriately rotated for any particular geometry.

In Fig. 7, we present the contributions to the interaction energy in long-range approximation for the equilibrium configuration of the  $\text{N}_2\text{H}^+-\text{H}_2$  complex. The potential is dominated by electrostatic interactions. The leading electrostatic term is proportional to  $\Theta^B q^A R^{-3}$  (see, Eq. (4)). There is a good agreement between the *ab initio* results and analytical representation for  $R > 15 a_0$ ; thus, we can use the long-range approximation for generating additional data ( $R$  larger than  $40 a_0$ ) with confidence. The data obtained using Eqs. (4) and (5) were, then, incorporated into the fitting procedure.

It is most convenient to expand, at each value of  $R$ , the interaction potential  $V(R, \theta, \theta', \varphi)$  in coupled spherical harmonics. For the interaction energy of two linear rigid rotors, we have used the expansion of Green,<sup>36</sup>

$$V(R, \theta, \theta', \varphi) = \sum_{l_1=0}^{16} \sum_{l_2=0}^6 \sum_{l=|l_1-l_2|}^{l_1+l_2} v_{l_1 l_2 l}(R) A_{l_1 l_2 l}(\theta, \theta', \varphi), \quad (6)$$

where  $v_{l_1 l_2 l}(R)$  are the radial functions and the basis functions  $A_{l_1 l_2 l}(\theta, \theta', \varphi)$  are products of associated Legendre polynomials  $P_{lm}$ ,

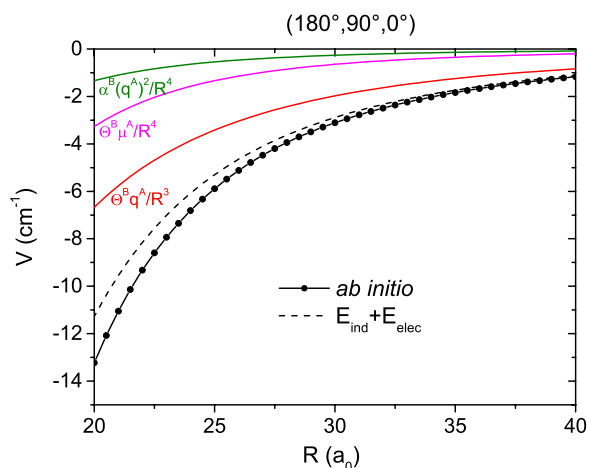


FIG. 7. Different contributions to the interaction energy of the  $\text{N}_2\text{H}^+-\text{H}_2$  system for equilibrium configuration. Energy is in  $\text{cm}^{-1}$ . Solid black line — CCSD(T)/aug-cc-pVTZ calculations; dashed black line — total interaction energy in long-range approximation; solid color lines — contributions to interaction energy from Eqs. (4) and (5).

$$A_{l_1 l_2 l}(\theta, \theta', \varphi) = \sqrt{\frac{2l_1 + 1}{4\pi}} \{ \langle l_1 0 l_2 0 | l_1 l_2 l 0 \rangle P_{l_1 0}(\theta) P_{l_2 0}(\theta') \\ + 2 \sum_m (-1)^m \langle l_1 m l_2 -m | l_1 l_2 l 0 \rangle \\ \times P_{l_1 m}(\theta) P_{l_2 m}(\theta') \cos(m\varphi) \}, \quad (7)$$

where  $\langle \dots | \dots \rangle$  is a Clebsch-Gordan coefficient. Here, indexes  $l_1, l_2$  are associated with the rotational motion of  $\text{N}_2\text{H}^+$  and  $\text{H}_2$ , accordingly, with the index  $l_2$  being even due to the homonuclear symmetry of hydrogen molecule.

At each intermolecular separation  $R$ , the *ab initio* points were fitted to expression (6) using the least squares method. Such expansion gives in total 238 radial expansion coefficients  $\nu_{l_1 l_2 l}(R)$ . Due to complicated  $R$ -dependence of the coefficients  $\nu_{l_1 l_2 l}(R)$ , they were represented using cubic splines. The final fitted potential reproduces the long-range part with an average relative error less than  $10^{-2}$ , the region of potential well  $\sim 10^{-1}$ , and the repulsive wall  $\sim 1$ . We carefully checked that for  $R \geq 40$  bohrs, there are only few nonzero coefficients and they have a smooth dependence with respect to  $R$ .

In order to evaluate the accuracy of our analytical representation, we computed the interaction potential for randomly selected geometries. In Fig. 8, we computed the deviations between *ab initio* values and analytical representation for these new values. As one can see, the agreement between the two sets of data is very good, the differences are generally lower than 1% in the potential well and in the repulsive part. The differences can be a bit larger for potential values  $\approx 0 \text{ cm}^{-1}$ . However, these differences will not significantly influence the scattering calculations.

### C. Features of the $\text{N}_2\text{H}^+-\text{H}_2$ PES

Figures 9–11 present some cuts of the PES.

The equilibrium structure was found for a T-shape configuration with the H atom of  $\text{N}_2\text{H}^+$  pointing towards the centre of mass of  $\text{H}_2$  ( $\theta = 180^\circ$ ,  $\theta' = 90^\circ$ , and  $\varphi = 0^\circ$ ). The corresponding distance between the centres of mass is  $R = 5.8 a_0$  with

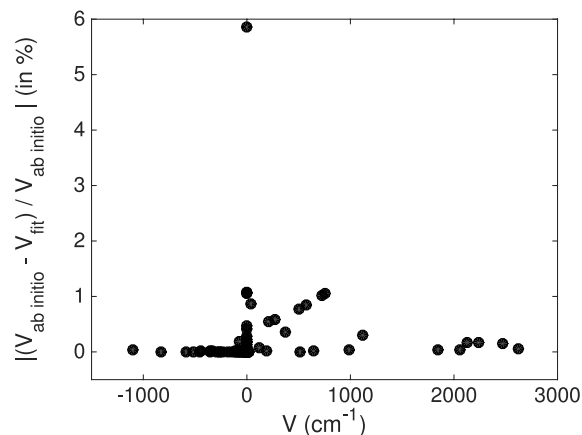


FIG. 8. Deviations (in %) between *ab initio* values and analytical representation for geometries randomly selected.

$\Delta E = -2531 \text{ cm}^{-1}$ . Such geometry is in a good agreement with the one obtained by Bieske *et al.*<sup>37</sup> in their *ab initio* study of the  $\text{N}_2\text{H}^+-\text{H}_2$  complex. Indeed, these authors found that the complex has a T-shaped minimum energy geometry with an  $\text{N}_2\text{H}^+-\text{H}_2$  intermolecular bond length of  $\approx 2.7$  bohrs. Such bond length compares relatively well with the present bond length of  $\approx 2.9$  bohrs. Bieske *et al.*<sup>37</sup> also optimized the  $r_{\text{NH}}$  distance in their calculations that explain part of the difference we observe. Their value for the dissociation energy ( $\approx 2000 \text{ cm}^{-1}$ ) cannot be directly compared with the present one since their value is corrected from zero-point energy. However, the two values are in reasonable agreement.

The well depth is far greater than the ones usually found for interstellar molecules interacting with  $\text{H}_2$ , even for the isoelectronic anionic  $\text{HCO}^+-\text{H}_2$  and  $\text{CN}^--\text{H}_2$  systems that present a well depth of approximately  $1500 \text{ cm}^{-1}$ <sup>38</sup> and  $1000 \text{ cm}^{-1}$ ,<sup>39</sup> respectively.

From Fig. 11 that shows the anisotropy of the interaction potential with respect to the  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  rotations, we observe a relatively strong anisotropy of the PES with respect to the two  $\theta$  and  $\theta'$  Jacobi angles. Therefore, we may expect that rotational state of  $\text{H}_2$  may influence the magnitude of the  $\text{N}_2\text{H}^+$  excitation cross sections.

Taking into account the large well depth, we also anticipate the need to use very large rotational basis sets for both

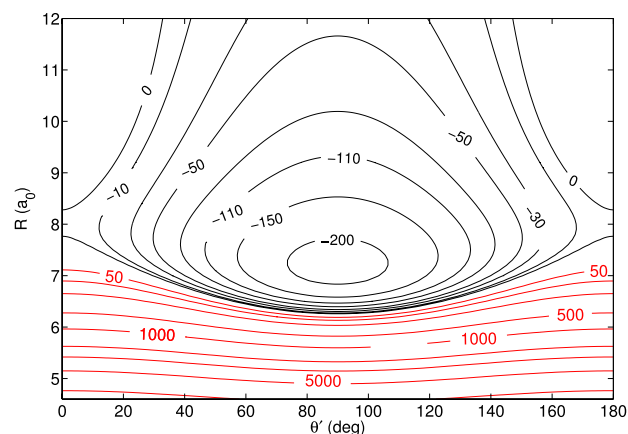


FIG. 9. Contour plot of the cut of the 4D PES for fixed  $\theta = 0^\circ$  and  $\varphi = 0^\circ$ . Energy is in  $\text{cm}^{-1}$ . Red contour lines represent repulsive interaction energies.

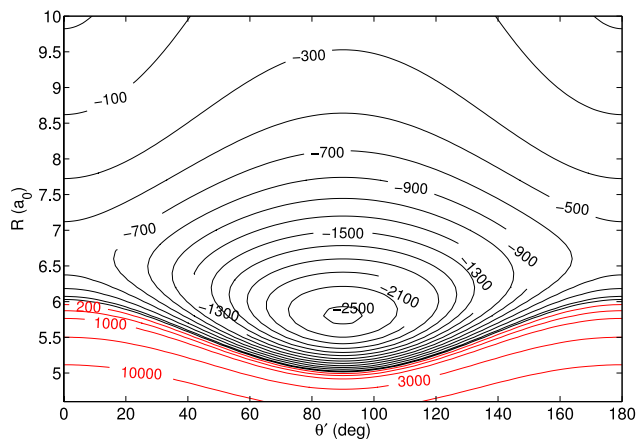


FIG. 10. Contour plot of the cut of the 4D PES for fixed  $\theta = 180^\circ$  and  $\varphi = 0^\circ$ . Energy is in  $\text{cm}^{-1}$ .

$\text{N}_2\text{H}^+$  and  $\text{H}_2$  to obtain full converged cross sections, even at low energies. For this reason, the AHR approach that reduces the 4D to a 2D problem will be explored below.

#### IV. REDUCED DIMENSIONAL POTENTIAL ENERGY SURFACES FOR COLLISIONAL EXCITATION STUDIES

Even using rigid rotor approximation, the study of the collisional excitation of  $\text{N}_2\text{H}^+$  by  $\text{H}_2$  remains very challenging from the dynamical calculations point of view. Taking into

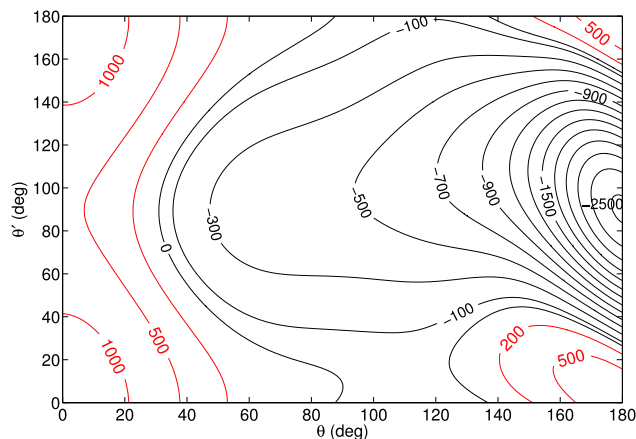


FIG. 11. Contour plot of the cut of the 4D PES for fixed  $\varphi = 0^\circ$  and  $R = 5.8 a_0$ . Energy is in  $\text{cm}^{-1}$ .

account the huge well depth as well as the small rotational constant of the  $\text{N}_2\text{H}^+$  molecule, converged scattering calculations require to include at least 28 and 6 levels in the rotational basis for  $\text{N}_2\text{H}^+$  and  $\text{H}_2$ , respectively. Scattering calculations with such a large number of channels would be prohibitive in terms of memory and CPU time. In addition, the large well depth also implies that converged collisional cross sections will have to be obtained by summing the partial cross sections over a very large number of total angular momentum even at low collisional energies.

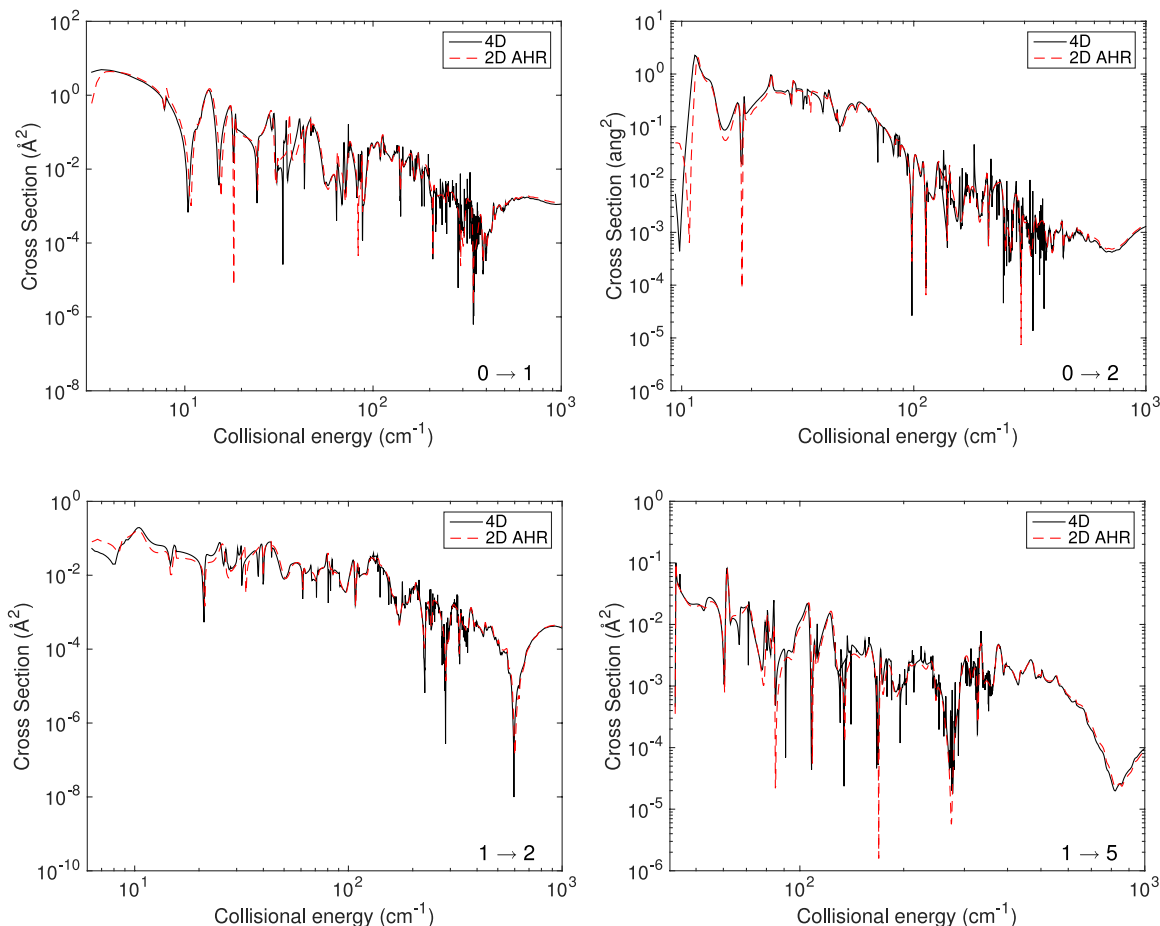


FIG. 12. Comparison of the  $j = 0 \rightarrow j' = 1$ ,  $j = 0 \rightarrow j' = 2$ ,  $j = 1 \rightarrow j' = 2$ , and  $j = 1 \rightarrow j' = 5$  cross sections (for total angular momentum  $J = 0$ ) for the  $\text{N}_2\text{H}^+ - \text{H}_2$  molecule in collision with para- $\text{H}_2$  as a function of the collision energy obtained from the full 4D PES (black lines) and the 2D AHR PES (red line).

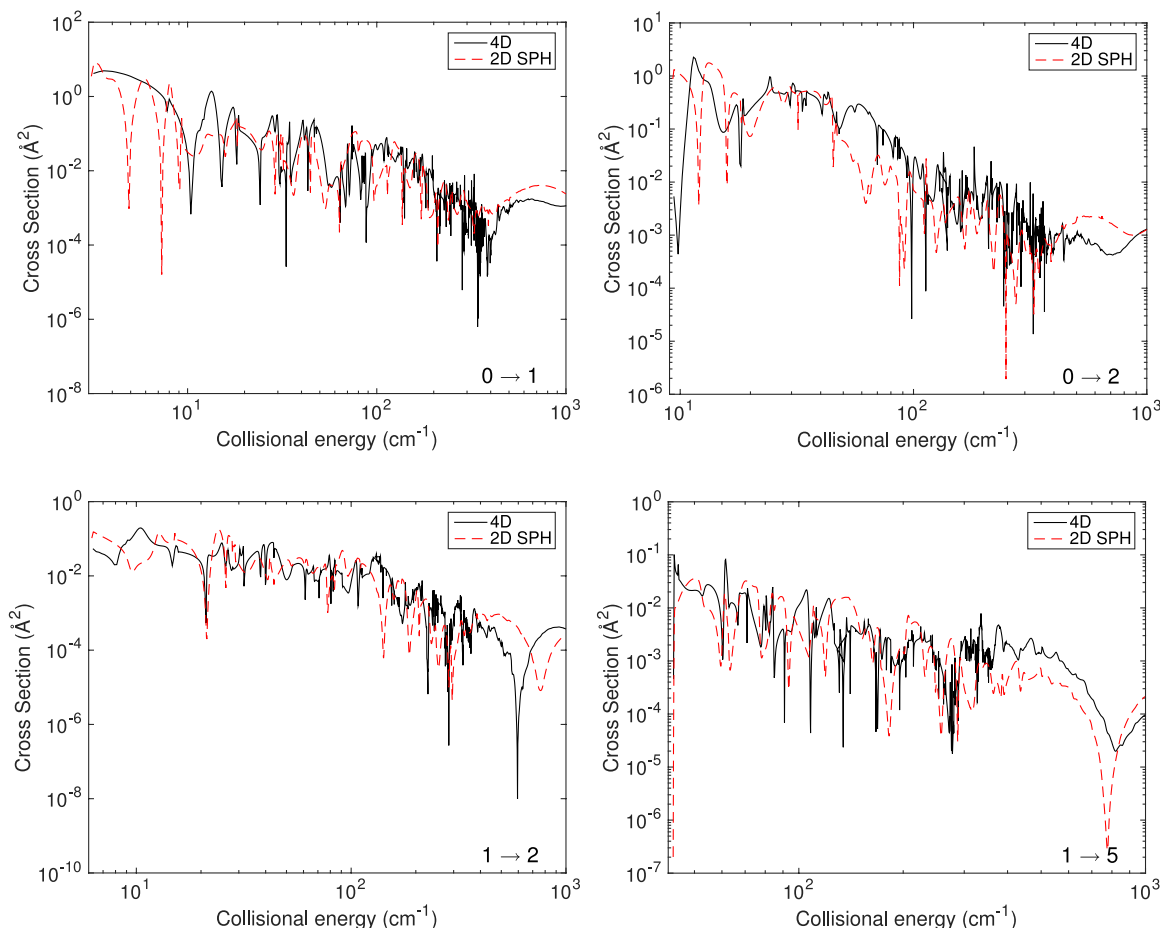


FIG. 13. Same as Fig. 12 for cross sections obtained from the full 4D PES (black lines) and the 2D SPH PES (red line).

It therefore seems reasonable to apply the “adiabatic-hindered-rotor” approach proposed by Hui Li *et al.*<sup>40</sup> and used successfully by Zeng *et al.*<sup>41</sup> for bound state calculations of H<sub>2</sub>O-para-H<sub>2</sub> and by Scribano *et al.*<sup>42</sup> for the rotational excitation study of H<sub>2</sub>O by collision with para-H<sub>2</sub>.

This so-called AHR approximation consists of a Born-Oppenheimer type separation of the fast rotational motion of H<sub>2</sub> from the slower motions associated with the other intermolecular degrees of freedom. Then, the N<sub>2</sub>H<sup>+</sup>-H<sub>2</sub> 4D-PES is reduced to a 2D-PES adapted to rotational excitation of N<sub>2</sub>H<sup>+</sup> by para-H<sub>2</sub> ( $j = 0$ ). For comparison, we have also considered a 2D-PES obtained by a simple-spherical average of the 4D-PES over H<sub>2</sub> orientations.<sup>14</sup>

We briefly summarize below the principle of this reduction dimensional scheme for N<sub>2</sub>H<sup>+</sup>-para-H<sub>2</sub> ( $j = 0$ ). In the Born Oppenheimer (or quasi-adiabatic scheme), the four coordinates ( $R, \theta, \theta', \varphi$ ) are separated out into “fast” rotational coordinates of hydrogen  $\mathbf{q} = \{\theta', \varphi\}$  and the “slow” other intermolecular coordinates  $\mathbf{Q} = \{R, \theta\}$ . This separation is governed by the high difference values of the rotational constants of the ion and of the hydrogen. Thus, following a similar approach used in electronic structure calculations, we compute at each grid point of the intermolecular coordinates  $\mathbf{Q}_p$  a two dimensional eigenvalue  $\mathcal{E}_n(\mathbf{Q}_p)$  for the  $(\theta', \varphi)$  coordinates of H<sub>2</sub>,

$$\hat{H}_{\text{H}_2} \Phi_n(\mathbf{q}; \mathbf{Q}_p) = \mathcal{E}_n(\mathbf{Q}_p) \Phi_n(\mathbf{q}; \mathbf{Q}_p), \quad (8)$$

where  $\hat{H}_{\text{H}_2}$  represents the Hamiltonian operator of hydrogen defined by its kinetic operator and by the 4D-intermolecular potential  $V(\mathbf{q}, \mathbf{Q})$ . The above equation defines the quasi-adiabatic (or Born Oppenheimer) potential  $\mathcal{E}_n(\mathbf{Q}_p)$  and the quasi-adiabatic wave function  $\Phi_n(\mathbf{q}; \mathbf{Q}_p)$  of fast coordinates, which both depend parametrically on the slow coordinates  $\mathbf{Q}$ .

In our near-adiabatic approximation, coupling between different adiabatic states and non-adiabatic derivative coupling terms is neglected.

Furthermore, we only consider the quasi-adiabatic ground state  $\Phi_0(\mathbf{q}; \mathbf{Q})$  wave function in the expansion of the full wave function. This approximation allows us to simplify the Born Oppenheimer Hamiltonian  $\hat{H}_{\text{BO}} = \langle \Phi_0 | \hat{H}_{4\text{D}} | \Phi_0 \rangle$ , which is then given by

$$\hat{H}_{\text{BO}} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 \mathbf{L}^2}{2\mu R^2} + \hat{T}_{\text{N}_2\text{H}^+} + \mathcal{E}_0(R, \theta), \quad (9)$$

where  $\mu$  is the reduced mass of N<sub>2</sub>H<sup>+</sup>-H<sub>2</sub>. This Hamiltonian describes the N<sub>2</sub>H<sup>+</sup> molecule interaction with a pseudo-atom, point-like X. Eq. (8) was solved with a FBR (Finite Basis Representation) method using a basis set of spherical harmonics  $Y_{j_2}^{m_2}(\mathbf{q})$  for the angular motion of hydrogen. This two-dimensional calculation was performed at each point of the two-dimensional  $\mathbf{Q}$  grid. This basis set was used to diagonalize the Hamiltonian of Eq. (8). The basis set was extended up to  $j_2^{\text{max}} = 4$ . For para-H<sub>2</sub>, only the even- $j_2$  values need to be considered.



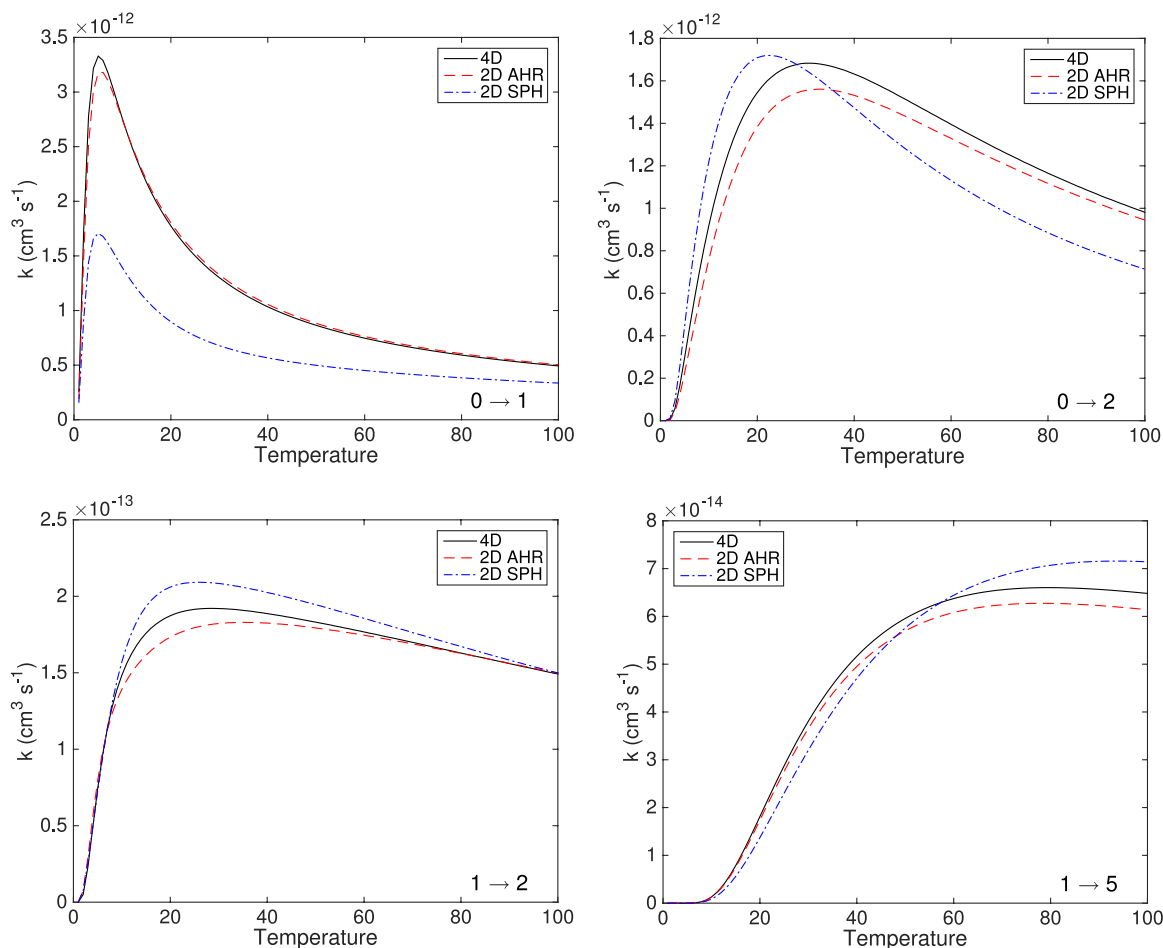


FIG. 14. Comparison of the  $j = 0 \rightarrow j' = 1$ ,  $j = 0 \rightarrow j' = 2$ ,  $j = 1 \rightarrow j' = 2$ , and  $j = 1 \rightarrow j' = 5$  temperature-dependent rate coefficients obtained with the full 4D PES (solid black lines) and with the 2D AHR and the 2D SPH PESs (dashed red and dashed-dotted blue lines, respectively).

The adiabatic energies computed in this way at the **Q** grid points were then fitted to an analytical form adapted to close-coupling calculations. The adiabatic potential  $V_{\text{AHR}}(R, \theta) = \mathcal{E}_0(R, \theta)$  was thus expanded as

$$V_{\text{AHR}}(R, \theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos \theta), \quad (10)$$

where  $P_{\lambda}(\cos \theta)$  are the Legendre polynomials. The grid points ( $\theta$ ) describing the angular coordinate of the pseudo-atom X relative to  $\text{N}_2\text{H}^+$  were chosen via a regular angular grid [ $0^\circ$ – $180^\circ$ ] for intermolecular distances  $R$  in the range 3–40  $a_0$ .

At each intermolecular distance, the interaction potential  $V_{\text{AHR}}(R, \theta)$  was then least-square fitted over a 19-term angular expansion following the procedure described by Werner *et al.*<sup>43</sup> The root-mean-square (rms) deviation between the analytical  $V_{\text{AHR}}$ -PES and the (averaged) *ab initio* data is 14  $\text{cm}^{-1}$  for the full set of 1330 geometries and 0.5  $\text{cm}^{-1}$  for the 1231 distances larger than 4.5 bohrs (when the highest part of the repulsive well is excluded).

The same fitting procedure was used to obtain the simple spherical-averaged PES ( $V_{\text{SPH}}$ ) defined as

$$V_{\text{SPH}}(R, \theta) = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta' \sin \theta' V(R, \theta, \theta', \varphi). \quad (11)$$

The latter approach has been frequently used over the most recent years. Its accuracy strongly depends on the anisotropy

of the PES with respect to the  $\text{H}_2$  rotation.<sup>14,44,45</sup> For molecular ions like  $\text{HCO}^+$ <sup>38,46</sup> or  $\text{CN}^-$ ,<sup>39</sup> the approximation has been found to be relatively accurate, the agreement with exact calculations being better than 20%-30%.

Note that both the present AHR and spherical averaged (SPH) PES can only be used to describe the collisional excitation of  $\text{N}_2\text{H}^+$  by para- $\text{H}_2(j = 0)$ . Its use to describe collisional excitation by  $\text{H}_2(j > 0)$  may lead to significant inaccuracies since  $\text{H}_2(j = 0)$  and  $\text{H}_2(j > 0)$  are generally different.<sup>44,47–50</sup>

## V. VALIDITY OF REDUCED DIMENSIONAL APPROACHES

To ascertain the error introduced by the use of the reduced dimension PESs, we have compared the  $\text{N}_2\text{H}^+$ –para- $\text{H}_2$  partial cross sections obtained from 2D (both AHR and SPH) and 4D PESs at a fixed total angular momentum  $J = 0$ . Close-coupling calculations for the collisional excitation of  $\text{N}_2\text{H}^+$  by para- $\text{H}_2(j = 0)$  were performed with the MOLSCAT code.<sup>51</sup> The  $\text{N}_2\text{H}^+$  and  $\text{H}_2$  energy levels were computed using the rotational constants of Sastry *et al.*<sup>52</sup> and of Huber and Herzberg,<sup>53</sup> respectively. In all these cases, to converge the calculations, the  $\text{N}_2\text{H}^+$  rotational basis set includes all target states up to  $j = 28$ . Cross sections based on the full 4D PES include the coupling with the  $j_2 = 2, 4$ , and 6 levels of  $\text{H}_2$ .

The  $j = 0 \rightarrow j' = 1$ ,  $j = 0 \rightarrow j' = 2$ ,  $j = 1 \rightarrow j' = 2$ , and  $j = 1 \rightarrow j' = 5$  cross sections, computed for a total angular momentum  $J = 0$  with the above AHR and SPH PES, are compared to “exact” scattering calculations based on the 4D PES on Figs. 12 and 13. As it can be seen, the agreement between the full 4D and the AHR results is excellent, with differences of less than a few percents between those data. Similar conclusions are drawn for all the transitions. The only difference comes from the presence of some resonances in the calculations based on the 4D PES that are not present or well reproduced when using the 2D-AHR surface. However, those resonances influence only moderately the magnitude of the rate coefficients as shown in Fig. 14 for the same transitions.

From Fig. 13, we also observed that the 2D-SPH calculations significantly differ from the exact calculations. The positions and magnitude of the resonances are very badly reproduced when using the SPH PES. Deviations also occur at high energies. Such differences are expected as found previously by Scribano *et al.*<sup>42</sup> for the rotational excitation study of H<sub>2</sub>O by collision with para-H<sub>2</sub> ( $j = 0$ ). As a consequence, the corresponding rate coefficients are in moderate agreement (20% up to a factor two, according to the transition and the temperature, see Fig. 14). However, it should be reminded that the rate coefficients have been computed from cross sections obtained from the only  $J = 0$  partial wave and that converged SPH rate coefficients with respect to  $J$  may be in better agreement with exact calculations since the impact of the resonances will be moderate. Nevertheless, differences will probably remain owing to the differences seen at high energies.

As a conclusion, the adiabatic scheme is a real alternative to the full 4D treatment as it leads to much faster calculations and allows for the use of large rotational basis of the target. Unfortunately, this method is not presently available for collisions with ortho-H<sub>2</sub> where the Born-Oppenheimer approximation breaks down (work in progress).

Accurate description of collisional cross sections with para-H<sub>2</sub> cannot be obtained from H<sub>2</sub> treated as a sphere despite, as already observed for collisions between H<sub>2</sub> and an ion, the SPH approach allows to get the correct order of magnitude of the rate coefficients.

## VI. CONCLUSION

This work presents a reliable 4-dimensional *ab initio* potential energy surface for the N<sub>2</sub>H<sup>+</sup>-H<sub>2</sub> system. Calculations were carried out at the CCSD(T) level with the aVTZ basis set of Woon and Dunning.<sup>28</sup> The global minimum occurs at 5.8 a<sub>0</sub> ( $\theta = 180^\circ$ ,  $\theta' = 90^\circ$ , and  $\varphi = 0^\circ$ ) with a well depth of  $-2530.86 \text{ cm}^{-1}$ . The interaction potential was then expanded in coupled spherical harmonics. A preliminary study of the reactive pathways shows that neglecting reactivity channels is valid for rotational excitation study at the typical temperatures of the ISM.

Considering the huge well depth as well as the small rotational structure of N<sub>2</sub>H<sup>+</sup>, it appears that fully converged scattering calculations that take into account both the rotational structures of the two molecules would be very challenging in terms of CPU time as well as in terms of required memory. Then, we have used the AHR approach proposed by Hui Li

*et al.*<sup>40</sup> to obtain reduced-dimension potential energy surfaces. Within this scheme, the dynamics of collisions with para-H<sub>2</sub> ( $j = 0$ ) is reduced from a 4D to a 2D problem. The comparison of cross sections and rate coefficients, computed for a total angular momentum  $J = 0$ , shows an excellent agreement between the 4D and the AHR results. This methodology will be used for the calculations of integral rotational excitation cross sections and rate coefficients by collisions with para-H<sub>2</sub>.

Preliminary calculations at very low temperatures and including the hyperfine structure have been already obtained recently.<sup>54</sup> The new rate coefficients seem to increase the simulated line intensities obtained from radiative transfer calculations compared to the use of previous rate coefficients. It is then crucial to extend these calculations to higher temperature in order to interpret N<sub>2</sub>H<sup>+</sup> observations in warmer regions. For collisional excitation with ortho-H<sub>2</sub> ( $j = 1$ ) collisional partner that also has to be considered for astrophysical applications, approximate calculations using the present PES will also be performed in order to evaluate the differences between para-H<sub>2</sub> ( $j = 0$ ) and ortho-H<sub>2</sub> ( $j = 1$ ) rate coefficients. Depending on the magnitude of the differences, specific ortho-H<sub>2</sub> ( $j = 1$ ) rate coefficients will then be computed. Approximate treatments (including the AHR treatment) will have to be explored in that case.

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